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Effect of nanocrystallite structure on the lower activation energy for Sm₂O₃-doped ZrO₂

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Abstract

Pure and 2 mol% Sm₂O₃-doped ZrO₂ nanopowders were synthesized via the precipitation method. The very lower activation energy (~25.979 kJ/mol) related to the bulk counterpart is observed for the grain growth within the calcination temperature range of 600-1000 °C. Experimental results show that two factors were contributed to the lower activation energy of grain growth. Firstly, the introduction of oxygen vacancies in nano-2SmSZ grain surface reduces the activation energy of the formation of necks between grains. Secondly, the rotation process between coherent grains has very lower activation energy or even a zero-kinetic barrier. © 2004 Elsevier B.V. All rights reserved.

Keywords: Crystal structure; Defect; X-ray diffraction; Zirconia

1. Introduction

Zirconia is an extremely important material with wideranging applications including as a high-performance transformation-toughened structural engineering ceramic [1] and as a solid electrolyte [2] (leading to applications as an oxygen sensor and as a fuel cell electrolyte). Zirconia has also been found application as a catalyst and catalyst support [3-5], especially when durability to chemical attack is required. Pure zirconia (ZrO_2) is monoclinic (m) at zero temperature (space group P21/c [6]); upon increase of the temperature (at zero pressure) the material transforms to tetragonal (t) and then to a cubic (c) fluorite structure (space groups P42/nmc and Fm3m, respectively) [7,8]. These phase transitions induce large volume changes and make the pure material unsuitable for applications. The addition of lower-valence oxides like CaO, MgO, or Y₂O₃ disfavor the m phase, stabilizing more symmetric structures with cubic and tetragonal symmetry [9]. Generally, the presence of the tetragonal phase at low temperature can be attributed to

several factors such as chemical effects (the presence of anionic impurities) [10], structural similarities between the tetragonal phase and the precursor amorphous phase [11,12], as well as particle size effects [13], which is based on the lower surface energy in the tetragonal phase compared to the monoclinic phase. Studies on new dopants capable of producing powders with improved physical and chemical properties are still of great interest. Doping of aliovalent oxides leads to both an increase in the oxygen vacancy concentration and an enhancement of the oxygenion conductivity, which enables the usage of this stabilized zirconia as an electrolyte in the fuel cells. Sm₂O₃ has been chosen being one of the materials under investigation in the field of oxygen-storage materials, the electrical conductivity materials and luminescent materials among the dopedzirconia materials [14], since Sm³⁺-doping induces the least distortion of the parent lattice.

Recently, Leite et al. [15] and Oliveira et al. [16] studied the grain growth process of nanocrystalline materials and proposed that the lower crystallite size of doped particles is due to the surface effect, with dopants preventing the formation of necks and the process of coalescence between particles. The similar phenomenon of reduced particle size for mixed ZrO₂-Sm₂O₃ oxide is also observed in our present results related to pure ZrO₂ particles obtained in

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the same way, and the very lower activation energy for 2SmSZ powders is also observed in this paper. Thus, the dope-induced small size effect must relate to the process of grain growth.

Based on the above reasons, not only synthesizing nanocrystalline oxide is important but also understanding its grain growth characteristics at the nanolevel is essential.

2. Experimental procedures

Mixed stock solution of Zr^{4+} and Sm^{3+} of 0.1 M concentrations with 2 mass% polyglycol (PEG, MWpeg = 20,000 g/mol) were prepared in the required proportions to attain pure and 2.0 mol% Sm_2O_3 -doped precursor solutions. These samples (denoted 0SmSZ and 2SmSZ) were prepared using the precipitation method by the slower addition of the NH₄OH (25%) solution until produce a desired pH value of 9.5 ± 0.2. The resulting precipitate was repetitious centrifugal washing with deionized water at 8000 n/min until a negative test for Cl⁻, and then continues centrifugal washing two times with anhydrous ethanol at 8000 n/min, and eventually dried at 100 °C for 24 h. Subsequently, the hydrous oxide was calcined for 2 h at different temperatures, always heating with a rate of 20 K/min to the desired temperatures.

Crystalline species in zirconia powders were identified using an X-ray diffraction (XRD: Model D/MAX-RB12X, Rigaku Co., Tokyo, Japan). The volume fraction of the monoclinic phase ($V_{\rm m}$) was determined by the empirical formula [17]

$$V_{\rm m} = [I_{\rm m}(111) + I_{\rm m}(11\overline{1})]/[I_{\rm m}(111) + I_{\rm m}(11\overline{1}) + I_{\rm t}(111)]$$
(1)

where $I_{\rm m}$ denotes the intensities of the monoclinic peaks, and $I_{\rm t}$ denotes the intensities of the tetragonal peaks. The mean crystallite sizes were calculated using the Scherrer and Warren equation [18]

$$D_{\rm t} = 0.9\lambda/(B^2 - b^2)^{1/2} \cos \theta_{\rm B}$$
(2)

where D_t is the mean crystallite size, $\lambda(0.154 \text{ nm})$ and θ_B denote the wavelength of X-rays and the Bragg diffraction angle, respectively, and *B* and *b* are the full width at half-maximum observed for the sample and the standard, respectively. The crystallite sizes and morphology of

0SmSZ and 2SmSZ samples at 600 °C calcination temperature were further confirmed by the Hitachi H-800 transmission electron microscope (TEM).

3. Results and discussion

An XRD of each sample is measured, and relative tetragonal volume fraction and crystalline size of each sample are shown in Table 1. Fig. 1 shows the XRD results of 0SmSZ samples under different calcination temperatures (600 and 800 °C). Fig. 2 shows the XRD results of 2SmSZ samples at different calcination temperatures (600, 700, 800, and 1000 °C). Fig. 3 shows the TEM result of 0SmSZ powders dried at 100 °C. Fig. 4 shows the TEM results of 0SmSZ(a) and 2SmSZ(b) powders at 600 °C calcination temperature, which agrees well with the crystalline sizes calculated by Scherrer formula.

The precipitation-synthesized nanosized OSmSZ and 2SmSZ powders are mainly tetragonal zirconia at 600 °C calcination temperature. At this temperature, the tetragonal volume fraction and crystalline size of 0SmSZ sample are 64.52 vol.% and 20.14 nm, and the tetragonal volume fraction and crystalline size of 2SmSZ sample are 100 vol.% and 16.48 nm, respectively. However, the tetragonal volume fraction decreased to 23.85 vol.% and crystalline size increased to 48.13 nm for 0SmSZ sample, and the tetragonal volume fraction reduced to 73.53 vol.% and crystalline size increased to 32.80 nm for 2SmSZ sample, at 800 °C calcination temperature. Calcination at higher temperatures (1000 °C) for 2SmSZ sample, the tetragonal volume fraction still contains 72.80 vol.% and crystalline size further increased to 50.77 nm. These results suggest that the growth in the average crystalline size is due to the aggregation of freestanding powder at higher calcination temperature, which also agrees well with the TEM observation of Figs. 3 and 4(a). As it can be observed from the change of crystalline size, the stabilization of tetragonal phase in the nanocrystalline 0SmSZ powders appears to be due to the critical size effect proposed by Garvie [13]. In Fig. 4(a), the distribution of crystalline size is not uniform, and the bigger particles (>30 nm) denote monoclinic zirconia while relatively smaller particles (<30 nm) denote tetragonal zirconia, which has occurred in previous study [19]. In Fig. 4(b), the distribution of

Table 1 Crystallite size and phase volume fraction at different calcination temperature (pH = 9.5 ± 0.2)

	600 °C		700 °C		800 °C		1000 °C	
	PC (vol.%)	CS (nm)	PC (vol.%)	CS (nm)	PC (vol.%)	CS (nm)	PC (vol.%)	CS (nm)
ZrO ₂ 2Sm–ZrO ₂	t(64.52) t(100)	20.14 16.48	- t(80.44)	_ 24.85	t(23.85) t(73.53)	48.13 32.80	- t(72.80)	- 50.77

PC, denotes phase volume fraction; CS, denotes crystalline size.



Fig. 1. Typical broad scan XRD patterns obtained reference- ZrO_2 powder calcination at different temperatures.

crystalline size is almost uniform, and all the crystalline sizes smaller than 30 nm. So those particles should be assigned to tetragonal zirconia according to the critical size effect [13]. At the same time, this fact has also been confirmed by the phase analysis of XRD results in Figs. 1 and 2. Thus, the stabilization of tetragonal phase in the nanocrystalline 2SmSZ powders, within the calcination temperature range of 600–1000 °C, is a result of doping the ZrO_2 lattice with Sm³⁺ cations.

The effect of calcination temperature on the average 2SmSZ nanocrystallite size is presented in Fig. 5(a). The average 2SmSZ nanocrystallite size increases from ~ 16 to 50 nm as the calcination temperature increases from 600 to 1000 °C. The limited growth in the average 2SmSZ nanocrystallite size with increasing calcination temperature indicates that the synthesized nanosized 2SmSZ powder contains hard aggregates of size ~ 50 nm under the given processing conditions.

To determine the activation energy (Q, kJ/mol) of grain growth within an agglomerated nanosized 2SmSZ powders, we replot Fig. 5(a) into Fig. 5(b). It assumes that the grain growth in the nanosized 2SmSZ, being a thermally activated

 $\frac{m}{10} \frac{m}{20} \frac{m}{30} \frac{m}{40} \frac{1000^{\circ}\text{C}}{50} \frac{1000^{\circ}\text{C}}{60} \frac{800^{\circ}\text{C}}{70} \frac{800^{\circ}\text{C}}{800^{\circ}\text{C}}$

Fig. 2. Typical broad scan XRD patterns obtained 2SmSZ powder calcination at different temperatures.



Fig. 3. TEM image of nanosized 0SmSZ powder at 100 $^\circ C$ temperature for 24 h via the precipitation method.

process, is dependent on the calcination temperature according to Eq. (3)

$$D_{\rm t} = D_0 \,\mathrm{e}^{(-Q/RT)} \tag{3}$$

where D_o and D_t denote the initial and final nanocrystallite sizes (nm), R is the gas constant (kJ/degree mol), T is the calcination temperature (K). Hence, the activation energy of grain growth can be obtained from the graph of Fig. 5(b) and is calculated to be ~25.979 kJ/mol, which is much lower than that observed for bulk zirconia (~580 kJ/mol) [20]. Similar observation has also been reported for other ceramics, namely ZnO [21], where the growth activation energy in the nanocrystalline grains is observed to be ~20 kJ/mol, while that for microcrystalline grains is observed to be ~275 kJ/mol. Moreover, this result accords well with the activation energy (~32–44 kJ/mol) of nano-SnO₂ growth [22], and this fact is further confirmed by



Fig. 4. TEM images of nanosized 0SmSZ (a) and 2SmSZ (b) powders after calculation at 600 $^{\circ}\rm C$ for 2 h via the precipitation method.



Fig. 5. (a) Effect of calcination temperature on the average nanocrystallite size for nanocrystalline 2SmSZ powder; (b) activation energy plot for nanocrystalline 2SmSZ.

the experimental result of ~ 40 kJ/mol activation energy for pure nano-ZrO₂ growth [23]. It is obviously that the very lower activation energy of grain growth appears to be a characteristic feature of nanocrystalline ceramic oxides, and the introduction of dopant further reduces the activation energy of grain growth.

How to elucidate the above phenomenon on the reduced activation energy? Based on the assumption of a hardsphere approximation, the instability of c-ZrO₂ originates from the close-packed oxygen ions in the fluoride structure, because of the ionic radii ratio, $R_{Zr4+}/R_{O2-} \approx 0.564$, is too small for eightfold coordination [24]. So the strong covalent nature of the Zr-O bond within the ZrO2 lattice favors a seven-fold coordination number, which is offered by the monoclinic crystal structure. As a result, monoclinic phase is the most stable crystal structure at room temperature for undoped ZrO₂ (assuming no particle size effect). When a low-valence cation dopant, such as Sm³⁺, is introduced into the ZrO₂ lattice, oxygen vacancies are created to maintain local electrical neutrality [9,25]. Due to the large size of Sm^{3+} cations relative to Zr^{4+} cations, the produced oxygen vacancies tend to be associated with Zr^{4+} cations [26], which reduce the effective coordination number of Zr⁴⁺ cations below seven. Furthermore, the crystal chemistry model also postulates that the dopant Sm^{3+} cations would also favor this eight-fold coordination with oxygen [27]. Hence, these effects are reflected in the stabilization of the tetragonal phase in 2SmSZ. The presence of large numbers of oxygen vacancies on grain surface, which mainly comes from the doping of Sm³⁺ and nanometer small size effect [28], makes the surface energy increase drastically and decrease the growth activation energy of nanoparticles.

The presence of vacancy defects must have an influence on the growth mechanism of grains, but the problem is more complicated. Leite et al. [29] thought that the grain-rotationinduced grain coalescence (GRIGC) mechanism [30] must be considered during the growth of nanocrystalline colloidal oxides. According to this model, the rotation of grains among neighboring grains results in a coherent grain–grain interface (the grains assume the same crystallographic orientation), which leads to the coalescence of neighboring grains via the elimination of common grain boundaries, thus

forming a single larger grain. During the calcination treatment of such a free-standing powder at low temperature, the increase in the particle size is mainly due to the elimination of the boundaries between the nanocrystallites within the hard aggregates [31]. At the same time, the bulk vacancies move toward grain surface [32] during the increase of calcining temperature. As a result, the very low activation energy value of \sim 25.979 kJ/mol observed in this study mainly comes from two aspects contribution for the grain growth behavior. First, the introduction of oxygen vacancies for nanograin reduces the activation energy of the formation of necks between grains. After this step, a rotation process, which presents very low activation energy or even a zero-kinetic barrier according to the GRIGC mechanism [29,30], may occur to decrease the angle of misorientation and change the grains' orientation. When the grains assume the same orientation, the grain boundary must migrate toward the smaller particle, resulting in a single larger crystalline nanocrystal.

4. Conclusions

Nanocrystalline pure and 2 mol% Sm₂O₃-doped ZrO₂ nanopowders were synthesized via the precipitation method using mixed 0.1 M ZrOCl₂·8H₂O and SmCl₃ precursor solution under the processing conditions of pH 9.5 \pm 0.2 and 2 wt% polyglycol (PEG, $MW_{peg} = 20,000$ g/mol). The very lower activation energy (~ 25.979 kJ/mol) is observed for the grain growth in the nanocrystalline 2SmSZ powder within the calcination temperature range of 600–1000 °C, and this fact was attributed to two factors. Firstly, the introduction of oxygen vacancies in nano-2SmSZ grain surface reduces the activation energy of the formation of necks between grains. After this step, a rotation process with very lower activation energy or even a zero-kinetic barrier may occur to decrease the angle of misorientation and change the grains' orientation. When the grains assume the same orientation, the grain boundary must migrate toward the smaller particle, resulting in a single larger crystalline nanocrystal.

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